Kinetics of the Ce^{3+}/BrO_2-Reaction in Sulfuric Acid Medium

H. D. Försterling, H. J. Lamberz, and H. Schreiber

Fachbereich Physikalische Chemie, Philipps-Universität Marburg,
Hans-Meerwein-Straße, D-3550 Marburg

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The reaction of Ce^{3+} with BrO_2 in sulfuric acid solution (which is the starting step in the inorganic reaction subset of the Belousov-Zhabotinsky-reaction) is followed spectroscopically in a reaction mixture containing BrO_2 at constant concentration. From first order kinetics (BrO_2 in excess) the rate constant for this reaction is evaluated.

Introduction

The autocatalytic formation of BrO_2 in the presence of cerium and bromate in sulfuric acid medium is of central importance in the theory of the Belousov-Zhabotinsky (BZ)-reaction [1–6]. The reaction is assumed to proceed by the following elementary steps [1]:

$$Ce^{3+} + BrO_2 + H^+ \rightarrow Ce^{4+} + HBrO_2 \qquad (R\,1)$$

$$HBrO_2 + HBrO_3 \rightleftarrows Br_2O_4 + H_2O \qquad (R\,2)$$

$$Br_2O_4 \rightleftarrows 2\,BrO_2 \qquad (R\,3)$$

$$2\,HBrO_2 \rightarrow HOBr + HBrO_3\,. \qquad (R\,4)$$

In all numerical simulations of the BZ-reaction carried out so far, only roughly estimated values for the rate constants $k_1 - k_4$ were used since direct experiments turned out to be difficult. Some years ago, we determined the ratios k_2/k_4 and k_3/k_{-3} by direct experiments on the $HBrO_2/HBrO_3$-reaction [7]. Furthermore, from studies of the $Ce^{3+}/HBrO_3$-reaction a good estimation of k_{-2} was obtained [8]. There are still discrepancies concerning the disproportionation of $HBrO_2$: $k_4 > 10^6\ mol^{-1}\ l\ s^{-1}$ on the basis of spectrophotometric measurements [9], $k_4 < 10^4\ mol^{-1}\ l\ s^{-1}$ on the basis of electrochemical measurements [10].

Up to now it was not possible to measure the rate of the starting step (R 1) directly. Field, Raghavan and Brummer [11] carried out experiments on reaction (R 1) by pulse radiolysis of $NaBrO_3$-solutions containing Ce^{3+}. In alcaline and neutral solution they found that Ce^{3+} does not react with BrO_2. Unfortunately, this technique cannot be applied in acid solution, and no extrapolation of their results to acid solutions is possible. The aim of this work is to present a direct method to follow the step (R 1) and to evaluate the rate constant k_1 in sulfuric acid medium.

In order to study (R 1), BrO_2 of known concentration must be formed in a sulfuric acid reaction mixture. Useful techniques may be the formation of BrO_2 by flashlight pulses [12] or by injections of $NaBrO_2$ [7] into bromate solutions in sulfuric acid. In both cases the concentration of BrO_2 is a complicated function of time, and it would be difficult to analyse the kinetics. Our procedure is based on a system with a constant concentration of BrO_2.

We start with the reaction of methanol with bromate [13]. The first step of this reaction is

$$CH_3OH + 2\,HBrO_3 \rightarrow HCOOH + 2\,HBrO_2 + H_2O\,. \qquad (R\,5)$$

This reaction is followed by the steps (R 2) – (R 4), and BrO_2 is formed as an intermediate (Figure 1). The maximum value of $[BrO_2]$ is reached within 50 s; from 50 to 200 s the concentration decreases linearly by only 10%. This time interval is sufficient long to perform experiments by injecting Ce^{3+} into the reaction mixture.

Of course, care must be taken that Ce^{3+} cannot be oxidized by other compounds also present in the solution. Consequently CH_3OH, HOBr and $NaBrO_2$ were injected into Ce^{3+}-solutions in sulfuric acid; within the experimental error of our spectropho-

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Reprint requests to Prof. Dr. H. D. Försterling, Fachbereich Physikalische Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-3550 Marburg.

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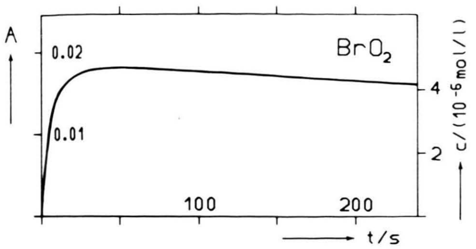

Fig. 1. Absorbance A at 550 nm (left hand scale) and concentration c (right hand scale) of BrO_2 as a function of time after the injection of 190 µl of a 0.5 m solution of CH_3OH (in 1 m H_2SO_4) into 220 ml of lm bromate in lm sulfuric acid. The absorbance was measured at 550 nm ($\varepsilon = 387$ mol^{-1} l cm^{-1} at 550 nm [14]).

tometer, no Ce^{4+} could be detected as a reaction product. This way a direct reaction of Ce^{3+} with CH_3OH, HOBr or $HBrO_2$ can be exluded. The only species left for a reaction with Ce^{3+} are BrO_2 and its dimer Br_2O_4.

Reagents

$NaBrO_3$ was purified by recrystallization from hot water [7]; H_2SO_4 (97%, Fluka), $Ce_2(SO_4)_3$ and CH_3OH (pa, Fluka) were used without further purification. The solutions were prepared with bidistilled water. The temperature was kept at 20±0.1 °C. All measurements were performed in lm sulfuric acid. Oxygen was excluded by bubbling N_2 through the reaction mixture.

Experiments

The experiments were carried out in a stirred reactor of 220 ml volume and 10 cm optical pathlength. The concentration of BrO_2 was followed by the absorbance at 550 nm, the concentration of Ce^{4+} at 400 nm using the dual wavelength technique [14]. Before starting the reaction, a solution of $NaBrO_3$ (lm) in sulfuric acid was bubbled with a stream of nitrogen for 20 minutes in order to exclude oxygen from the reaction mixture. 190 µl of a solution of CH_3OH (0.5 m) in lm sulfuric acid (leading to an initial concentration $[CH_3OH]_0 = 4.3 \cdot 10^{-4}$ m) were injected, and the formation of BrO_2 was monitored (signal wavelength 550 nm, reference 670 nm). As soon as the BrO_2-concentration was nearly constant, 180 µl of a solution of $Ce_2(SO_4)_3$ (0.001 m) in sulfuric acid (leading to an initial concentration $[Ce^{3+}]_0 = 1.6 \cdot 10^{-6}$ m) were injected, and the formation of Ce^{4+} was monitored (signal wavelength 400 nm, reference 550 nm).

Both signals are plotted in Figure 2. It is clearly to be seen from Fig. 2a, that the BrO_2-concentration (which is proportional to the absorbance at 550 nm) is constant within 1% during the experiment (which is finished after 10 s). The interpretation of Fig. 2b is more complicated, since the signal increases linearly before the injection of Ce^{3+}. The reason for this behaviour is that the $HBrO_2$ formed during the reaction disproportionates into HOBr and $HBrO_3$ (R 4); this way HOBr accumulates in the solution giving rise to an additional change of the absorbance at 400 nm. In order to evaluate the increase of the Ce^{4+}-concentration, the contribution of HOBr to the absorbance has to be subtracted as indicated in Figure 2b.

According to (R 1) a first order kinetics for Ce^{4+} is expected at constant BrO_2 concentration:

$$d[Ce^{4+}]/dt = k_1'[Ce^{3+}] = k_1'(c_0 - [Ce^{4+}]) \quad (1)$$

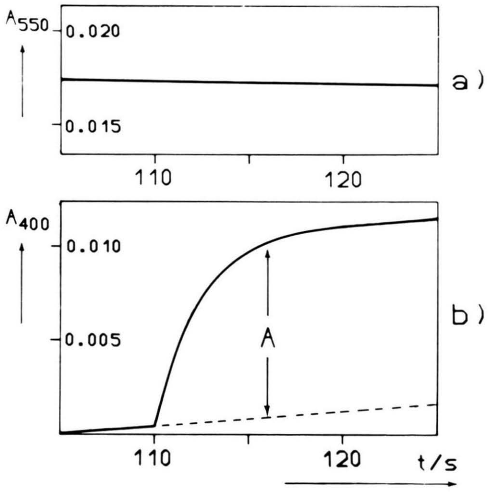

Fig. 2. Change of the absorbance A as a function of time after the injection of 190 µl of a 0.5 m solution of CH_3OH into the bromate solution (case a in Table 1). At time $t_0 = 110$ s 180 µl of a solution of $Ce_2(SO_4)_3$ (concentration 0.001 mol/l) were injected. a) Wavelength 550 nm (absorbance A_{550} of BrO_2); b) Wavelength 400 nm (absorbance A_{400} of Ce^{4+} and of HOBr); the absorbance A of Ce^{4+} was obtained as indicated.

c_0 being the initial concentration of Ce^{3+} and $k_1' = k_1\,[BrO_2]$ the first order rate constant. Using the relation

$$A = d\varepsilon\,[Ce^{4+}] \tag{2}$$

for the absorbance of Ce^{4+} (ε = extinction coefficient at 400 nm) we obtain by integration

$$\ln((A_\infty - A)/A_\infty) = -\,k_1'\,t \tag{3}$$

(A_∞ = absorbance at the end of the reaction).

Results

For the experiment described above the left hand side of (3) is plotted as a function of time in Fig. 3 (curve a). The plot demonstrates that the reaction is first order indeed, and the first order rate constant $k_1' = 0.46\ s^{-1}$ is obtained. Since $[BrO_2] = 4.7 \cdot 10^{-6}$ m in this experiment, $k_1 = 0.97 \cdot 10^5\ mol\ l\ s^{-1}$ is calculated. In order to check that BrO_2 is actually the only species reacting with Ce^{3+} the experiment was repeated at different concentrations of BrO_2 which were obtained by injecting different amounts of CH_3OH (down to an initial concentration $[CH_3OH] = 4 \cdot 10^{-5}$ m) into the bromate solution. The results are given in Table 1 (case f is also plotted in Fig. 3), and k_1' is plotted as a function of $[BrO_2]$ in Figure 4. A straight line is obtained indicating that k_1' depends linearly on $[BrO_2]$. If there were a direct reaction of Ce^{3+} with the dimer Br_2O_4 (which is in a fast equilibrium with BrO_2 according to (R 3)), the first order rate constant k_1' is expected to increase with $[BrO_2]^2$. This way we conclude that (R 1) is the actual reaction of Ce^{3+} in the system and that no direct reaction between Ce^{3+} and Br_2O_4 occurs.

Table 1. First order rate constants k_1' at different concentrations of BrO_2 (which were obtained by using different concentrations of methanol and by starting (R 1) at different times t_0 after the injection of methanol).

	$[CH_3OH]$ 10^{-4} m	t_0 [s]	$[BrO_2]$ 10^{-6} m	$[Ce^{3+}]_0$ 10^{-6} m	k_1' $[s^{-1}]$
a	4.3	110	4.7	1.6	0.46
b	4.0	170	3.9	0.4	0.40
c	4.0	270	3.5	0.8	0.34
d	4.0	300	3.2	0.4	0.31
e	0.40	70	2.3	1.6	0.22
f	0.40	180	2.1	1.6	0.19
g	0.40	80	2.4	0.8	0.25

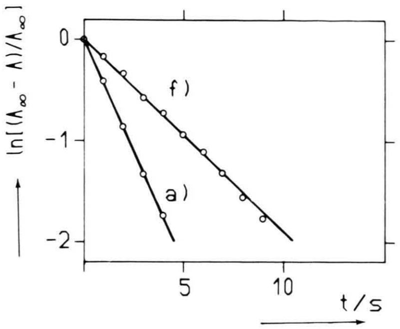

Fig. 3. Evaluation of the first order rate constants k_1' from (3). The time t is measured from the Ce^{3+}-injection. Curves a and f correspond to Table 1.

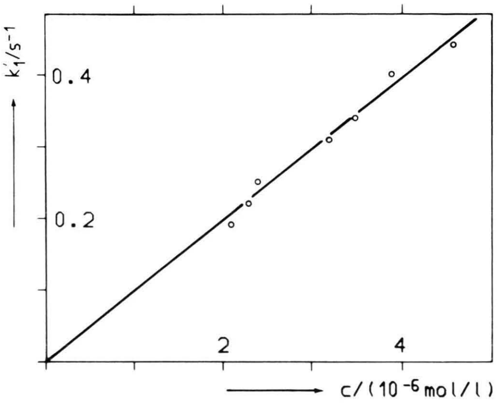

Fig. 4. First order rate constants k_1' (see Table 1) as a function of the concentration c of BrO_2.

From the slope of the straight line in Fig. 4 the rate constant $k_1 = (1.0 \pm 0.05) \cdot 10^5\ mol^{-1}\ l\ s^{-1}$ is obtained.

Discussion

The value $k_1 = 1 \cdot 10^5\ mol^{-1}\ l\ s^{-1}$ obtained in this work is larger than the value $k_1 = 0.65 \cdot 10^5\ mol^{-1}\ l\ s^{-1}$ estimated by us earlier indirectly from the study of the Ce^{3+}/bromate-reaction [8] and considerably smaller than the value $k_1 = 6.5 \cdot 10^5\ mol^{-1}\ l\ s^{-1}$ used so far [1–5, 15]. The error limit of our value may be larger than 5% as given above, since there is some uncertainty in the value of the extinction coefficient of BrO_2. A value $\varepsilon_{max} = 1000\ mol^{-1}\ l\ cm^{-1}$ was obtained by pulse radiolysis [16] and by flashlight [17] experiments, but our experiments on the $HBrO_2/HBrO_3$-reaction [7] indicate that ε_{max} might be smal-

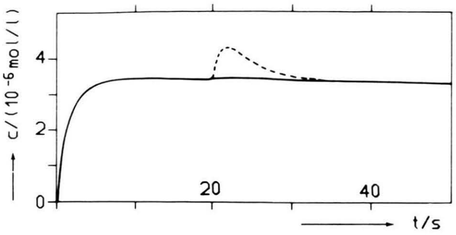

Fig. 5. Concentration c of BrO_2 calculated from the reactions (R 1) to (R 5). At $t = 20$ s the reaction (R 1) was started by switching the rate constant k_1 from 0 to $1.0 \cdot 10^5$ mol^{-1} l s^{-1}. Initial concentration of $CH_3OH = 4 \cdot 10^{-4}$ mol/l. Values of the rate constants k_2 to k_5 see text. The rate equations were integrated by Gear's method [18, 19]. – Straight line: $[Ce^{3+}]_0 = 1.6 \cdot 10^{-6}$ mol/l; Dashed line: $[Ce^{3+}]_0 = 6.0 \cdot 10^{-5}$ mol/l.

ler by 20%. Of course, this difference would affect the value of k_1 directly (leading to a decrease by 20%).

From Fig. 2 it is to be seen that $[BrO_2]$ is constant within 1% during the experiment although $[BrO_2]$ is larger than $[Ce^{3+}]_0$ only by a factor of 3. Apparently, the system works as a buffer for BrO_2. How the buffer system works is easily to be seen by simulation of (R 1) to (R 5) using $k_1 = 1.0 \cdot 10^5$ mol^{-1} l s^{-1} as determined above, $k_2 = 200$ mol^{-1} l s^{-1}, $k_{-2} = 5$ s^{-1}, $k_3 = 2.1 \cdot 10^3$ s^{-1}, $k_{-3} = 1.4 \cdot 10^9$ mol^{-1} l s^{-1}, $k_4 = 4 \cdot 10^7$ mol^{-1} l s^{-1} [8] and $k_5' = k_5[HBrO_3] = 3.8 \cdot 10^{-3}$ s^{-1} [13]. The simulation was started with $k_1 = 0$, and at $t = 20$ s (R 1) was switched on by changing k_1 into $1 \cdot 10^5$ mol^{-1} l s^{-1}. The results are plotted in Figure 5. If $[Ce^{3+}]_0 = 1.6 \cdot 10^{-6}$ m (this is the highest concentration used in our experiments), the curve for BrO_2 looks nearly the same as in the absence of cerium. If $[Ce^{3+}]_0 = 6.0 \cdot 10^{-5}$ m (in this case the cerium concentration is about ten times larger than $[BrO_2]$), the concentration of BrO_2 increases significantly after (R 1) was started and reaches a maximum value 28% larger than the starting level. The increase is due to the reactions (R 1) to (R 3), since more BrO_2 is produced by (R 2) and (R 3) than can be consumed by (R 1). In the course of the decay of Ce^{3+} due to (R 1) the concentration of BrO_2 decreases again down to the starting level. This behaviour can also be verified experimentally. In our procedure to determine the rate constant k_1 the concentration of Ce^{3+} was small enough, hence $[BrO_2]$ was sufficiently constant during the experiment.

In our evaluation of k_1 the inverse reaction (R-1)

$$Ce^{4+} + HBrO_2 \rightarrow Ce^{3+} + BrO_2 + H^+ \qquad \text{(R-1)}$$

which was investigated by Thompson [20] and Lamberz [9] was not taken into account although $HBrO_2$ is present in our experiment. A closer inspection of Fig. 2 reveals that the absorbance A is about 20% lower than expected for the formation of $1.6 \cdot 10^{-6}$ m Ce^{4+}. The same result is obtained if $Ce(SO_4)_2$ is injected into the same bromate-CH_3OH-mixture. These observations indicate that the reactions (R 1) and (R-1) lead to an equilibrium. Nevertheless, immediately after the injection of Ce^{3+} the reaction (R 1) will dominate; this is in accordance with the fact that reasonable first order plots are obtained (Fig. 3). From this result we conclude that the establishment of an equilibrium will not change our value k_1 significantly. Of course, (R-1) must be included in a refined investigation.

Using our technique, the reaction of BrO_2 with other catalysts important in the Belousov-Zhabotinsky rection (like Mn^{2+}, ferroin, Ru-dipyridyl) may be investigated.

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